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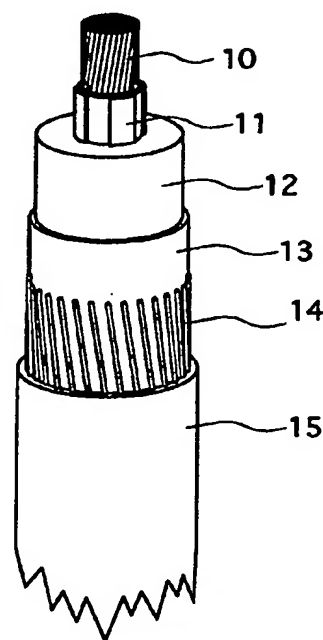
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| (54) Title: A DIELECTRIC GELLING COMPOSITION, A METHOD OF MANUFACTURING SUCH A DIELECTRIC GELLING COMPOSITION AND AN ELECTRIC DC-CABLE COMPRISING AN INSULATION SYSTEM IMPREGNATED WITH SUCH A DIELECTRIC GELLING COMPOSITION (57) Abstract A dielectric gelling composition, exhibiting a thermo-reversible liquid-gel transition at a transition temperature, T_t , wherein the gel comprises an oil and a gelator with a block copolymer comprising an olefin based block and at least one further block comprising aromatic rings in its backbone structure, wherein each one of the two blocks has a molecular weight of more than 3000 g/mole, and the block with aromatic rings in its backbone structure exhibits a rigid backbone structure and a temperature dependent solubility in the oil, is disclosed. The gelling composition is produced by preparing the block copolymer by means of a condensation reaction and subsequently adding the resulting copolymer to an oil at a temperature above the transition temperature of the gelling composition. The gelling composition is used as an impregnant in an insulated direct current cable having at least one conductor and an impregnated insulation system. The insulation system comprises a solid electrically insulating dielectric part with a porous, fibrous and/or laminated structure impregnated with a dielectric gelling composition. | | |



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A DIELECTRIC GELLING COMPOSITION, A METHOD OF MANUFACTURING SUCH A DIELECTRIC GELLING COMPOSITION AND AN ELECTRIC DC-CABLE COMPRISING AN INSULATION SYSTEM IMPREGNATED WITH SUCH A DIELECTRIC GELLING COMPOSITION

TECHNICAL FIELD

The present invention relates to a dielectric gelling composition comprising an electrical insulation oil with additions of a gelator comprising a polymer compound. With gelator is in this application meant a compound, a blend or system of compounds or blends which when added to an oil interacts to transform the oil from a liquid state to a gelled state, comprising a gelled state, wherein the oil in the gelled state comprises a three dimensional structure that imparts a high viscosity and elasticity to the gelled oil. In particular the invention relates to such an oil based gelling composition that exhibits a thermo-reversible transition between the free flowing liquid state and the gelled state, a thermo-reversible liquid-gel transition.

The present invention relates in another aspect to an insulated electric device, such as a DC-cable, with an insulation system comprising such a dielectric gelling composition with a thermo-reversible liquid-gel transition.

BACKGROUND ART

Electrical insulation oils and other dielectric fluids are used in electric insulation systems for devices such as transformers, capacitors, reactors, cables and the like. The dielectric fluids are typically used in combination with a porous, fibrous and or laminated solid part, which is impregnated with the dielectric fluid. The active part of an impregnated insulation is the solid part. The oil protects the insulation against moisture pick-up and fills all pores, voids or other interstices, whereby any dielectrically weak air in the insulation is replaced by the oil. Impregnation is typically a time consuming and delicate

process carried out after the solid part of the insulation have been applied and needs to be carefully monitored and controlled. For example the impregnation of a DC-cable intended for a long distance transmission of electric power, where several kilometres of a cable is treated, typically exhibit a process cycle time extending over days or weeks or even months. In addition, this time consuming impregnation process is made according to a carefully developed and strictly controlled process cycle with specified ramping of both temperature and pressure conditions in the impregnation vessel used during heating, holding and cooling to ensure a complete and even impregnation of the fiber-based insulation. The impregnation of other insulation systems comprising dielectric fluids such as transformers, capacitors and the like is, although not as time consuming as the impregnation of a DC-cable, a sensitive process and specific demands are put on the impregnant, the medium to be impregnated and the process variables used for impregnation.

To ensure a good impregnation result, a fluid exhibiting a low-viscosity is desired. The fluid shall also preferably be viscous at operation conditions for the electrical device to avoid migration of the fluid in the porous insulation. Darcy's law (1) is often used to describe the flow of a fluid through a porous or capillary medium.

$$(1) : \quad v = \frac{k \Delta P}{\mu L}$$

In this law v is the so called Darcy velocity of the fluid, defined as the volume flow divided by the sample area, k is the permeability of the porous medium, ΔP is the pressure difference across the sample, μ is the dynamical viscosity of the fluid and L is the thickness of the sample. The flow velocity of a fluid within a porous medium is essentially reciprocally proportional to the viscosity. A fluid exhibiting a low-viscosity or a highly temperature dependent viscosity at operating temperature will have a tendency to migrate under the influence of temperature fluctuations naturally occurring in an electric device during operation and also due to any temperature gradient building up across a conductor insulation in operation and might result in unfilled voids being formed in the insulation. Temperature fluctuations and temperature gradients are present in a high-voltage DC cable thus any problem associated with migration of the dielectric fluid must be carefully considered. Unfilled voids or other unfilled interstices or pores in an insulation operating under an

electrical high-voltage direct current field constitute deficiencies where space charges tend to accumulate. Accumulated space charge might under unfavourable conditions initiate dielectric breakdown through discharges which will degrade the insulation and ultimately might lead to its breakdown. The ideal dielectric fluid should exhibit a low-viscosity under impregnation and be highly viscous under operation conditions.

Conventional dielectric oils used for impregnating a porous, fibrous or laminated conductor insulation in an electric device such as a DC cable exhibit a viscosity that decreases essentially exponential as the temperature increases. The impregnation temperature must therefore be substantially higher than the operation temperature to gain the required decrease in viscosity due to the low temperature dependence of the viscosity at high temperatures. In comparison the temperature dependence of the viscosity at temperatures prevailing during operation conditions, is high. Small variations in impregnation or operation conditions affect the performance of the dielectric fluid and the conductor insulation. Oils are therefore selected such that they are sufficiently viscous at expected operation temperatures to be essentially fully retained in the insulation also under the temperature fluctuations that occur in the electric device during operation. The retention shall also be essentially unaffected of any temperature gradient building up over an insulation. This typically leads to a high impregnation temperature being used to ensure that the insulation will be essentially fully impregnated. However, a high impregnation temperature is disadvantageous as it risks affecting the insulation material, the surface properties of the conductor and promoting chemical reactions within and between any material present in the device being impregnated. Also energy consumption during production and overall production costs are negatively affected by a high impregnation temperature. Another aspect to consider is the thermal expansion and shrinkage of the insulation which implies that the cooling must be controlled and slow, adding further time and complexity to an already time consuming and complex process. Other types of oil impregnated cables employ a low viscosity oil. However these cables then comprise tanks or reservoirs along the cable or associated with the cable to ensure that the cable insulation remains fully impregnated upon thermal cycling experienced during operation. With these cables, filled with a low viscosity oil, there is a risk for oil spillage from a damaged cable. Therefore, an oil exhibiting a highly temperature dependent viscosity with a high viscosity at operating temperature is preferred.

To impart a suitable increased temperature dependency in the viscosity for a conventional mineral oil, it is known to add and dissolve a polymer, e.g. polyisobuthene, in the oil. This can only be achieved for highly aromatic oils, but oils of this kind typically exhibit, poorer electric properties in comparison with more naphthenic oils. These latter are oil types suitable for use in electric insulations. A more aromatic oil must typically be treated with bleaching earth to exhibit acceptable electric properties. Such processing is costly and there is a risk that small sized clay-particles remain in the oil if not a careful filter- or separation-processing is carried out after this treatment. Alternatively an oil as disclosed in US-A-3 668 128 comprising additions of from 1 up to 50 percent by weight of an alkene polymer with a molecular weight in the range 100-900 derived from an alkene with 3, 4 or 5 carbon atoms, e.g. polybutene can be chosen for its low viscosity at low temperatures. This oil exhibits a low viscosity at low temperatures, good oxidation resistance and also good resistance to gassing, i.e. the evolution of hydrogen gas which might occur, especially when an oil of low aromatic content, as the oil suggested in US-A-3 668 128, is exposed to electrical fields. However, the oil according to the disclosure in US-A-3 668 128, although offering a major advance on the traditional electrical insulating oil for impregnation of fibrous or laminated insulations, still suffers the risk of oil migration caused by temperature fluctuations and/or temperature gradient building up under operation as the low viscosity oil is typically not retained during operation at elevated temperatures.

The earlier not yet published International Patent Application PCT/SE97/01095 discloses a DC-cable impregnated with a gelling dielectric fluid, such as an oil. The dielectric fluid comprises a gelling polymer additive that imparts to the fluid a thermo-reversible transition between a gelled state at low temperatures and an essentially Newtonian easy flowing state at high temperatures. This substantial transition in viscosity occurs over a limited temperature range. The fluid and the gelling polymer additive are matched to impart a thermo-reversible gelling behavior with a liquid-gel transition range to the fluid to suit the desired properties both during impregnation and operation. The fluid is, at high temperatures, in a liquid state and exhibits the viscosity of an easy flowing Newtonian fluid. At low temperatures the fluid is in a gelled state, with a viscosity of a highly viscous, elastic gel. The transition temperature is determined by the selection of fluid and additive and the content of additive. Such a cable exhibits a substantial potential for reduction of the time period needed for impregnation but it still requires a strictly controlled temperature cycle during

impregnation. The gelling polymer additive and the dielectric fluid are matched or optimized to, in the best way, meet the typically conflicting demands during impregnation and use of the cable. There is in the art a strong desire to reduce impregnation temperatures and at the same to increase the current densities in the DC-cables. Increased current densities will, while using same conductors and same conductor dimensions, lead to increased operation temperatures in the DC-cable. Meeting both these conflicting demands will further reduce the gap between the impregnation temperature and operation temperature. Consequently it will be harder to match the specific demands even with sophisticated gelling systems. It must be remembered that not only shall essentially all voids and interstices of the cable insulation be filled by the fluid but the fluid shall also be retained in this insulation as the temperature fluctuates and temperature gradients build up during operation. Suitable gelling systems, comprising oils and polymers, for other purposes are discussed in the European Patent Publication EP-A1-0 231 402. This publication discloses a gel-forming compound with slow forming and thermally reversible gelling properties intended to be used as an encapsulant to ensure a good sealing and blocking of any interstices in a cable comprising an all solid insulation, such as an extruded polymer based insulation. The slow-forming thermally reversible gelling compound comprises an admixture of a polymer to a naphtenic or paraffinic oil, and also embodiments using further admixtures of a co-monomer and/or a block copolymer to an oil are considered suitable as encapsulant due to their hydrofobic nature and the fact that they can be pumped into the interstices at a temperature below the maximum service temperature of the encapsulant itself. Similar gel-forming compounds for the same purpose, i.e. the use as encapsulant to block water from entering and spreading longitudinal in a cable are also known from the European Patent Publications, EP-A1- 0 058 022 and EP-A1-0 586 158.

Thus it is desirable to provide a dielectric gelling composition with a thermo-reversible liquid-gel transition at a high temperature, and within a narrow temperature range. The gelling composition shall exhibit properties whereby the impregnation can be enhanced and the impregnation time shortened. It shall exhibit a high viscosity at the temperature range within which the device is designed to operate, thereby reducing the risks for migration and formation of voids upon thermal cycling and/or under thermal gradients. The volume changes upon thermal cycling shall be reduced. In particular importantly, the shrinkage upon cooling after impregnation and any problems associated with such shrinkage shall be reduced. Further

the gelling composition shall exhibit such thermal, mechanical and electric properties and stability in these properties such that it opens for an increase in load, i.e. an increase in both operation voltages and current densities used in the device.

Many of the first electrical supply systems for transmission and distribution of electrical power were based on DC technology. However, these DC systems were rapidly superseded by systems using alternating current, AC. The AC systems had the desirable feature of easy transformation between generation, transmission and distribution voltages. The development of modern electrical supply systems in the first half of this century was exclusively based on AC transmission systems. By the 1950s there was a growing demand for long transmission schemes and it became clear that in certain circumstances there could be benefits by adopting a DC based system. The foreseen advantages include a reduction of problems encountered in association with the stability of the AC-systems, a more effective use of equipment as the power factor of the system is always unity and an ability to use a given insulation thickness or clearance at a higher operating voltage. Against these very significant advantages has to be weighed the cost of the terminal equipment for conversion of the AC to DC and for inversion of the DC back again to AC. However, for a given transmission power, the terminal costs are constant and therefore, DC transmission systems are economical for schemes involving long distances, such as for systems intended for transmission from distant power plants to consumers but also for transmission to islands and other schemes with transmission distances where the savings in the transmission equipment exceed the cost of the terminal plant. An important benefit of DC operation is the virtual elimination of dielectric losses, thereby offering a considerable gain in efficiency and savings in equipment. The DC leakage current is of such small magnitude that it can be ignored in current rating calculations, whereas in AC cables dielectric losses cause a significant reduction in current rating. This is of considerable importance for higher system voltages. Similarly, high capacitance is not a penalty in DC cables. A typical DC-transmission cable includes a conductor and an insulation system comprising a plurality of layers, such as an inner semi-conductive shield, an insulation body and an outer semi-conductive shield. The cable is typically complemented with casing, reinforcement etc, to withstand water penetration and any mechanical wear or forces during, production installation and use. Almost all the DC cable systems supplied so far have been for submarine crossings or the land cable associated with them. For long crossings the mass-impregnated solid paper

insulated type cable is chosen because there are no restrictions on length due to pressurizing requirements. It has to date been supplied for operating voltages of 450 kV. These voltages are likely to be increased in the near future. To date an essentially all paper insulation body impregnated with a electric insulation oil has been used but application of laminated material such as a polypropylene paper laminate is being pursued. As in the case of AC transmission cables, transient voltages is a factor that has to be taken into account when determining the insulation thickness of DC cables. It has been found that the most onerous condition occurs when a transient voltage of opposite polarity to the operating voltage is imposed on the system when the cable is carrying full load. If the cable is connected to an overhead line system, such a condition usually occurs as a result of lightning transients. A commercially available insulated electric DC-cable such as a transmission or distribution cable designed for operation at a high voltage, i.e. a voltage above 100 kV, is typically manufacture by a process comprising the winding or spinning of a porous, fibrous and/or laminated solid insulation based on cellulose or paper fiber and the impregnation of this cable. The impregnation process, the times and controlled processing involved have already been described in the foregoing.

Thus it is desirous to provide an insulated DC-cable with an electrical insulation system that ensures stable dielectric properties also when operating at high operation temperatures close to the impregnation temperature and/or under conditions where the insulation during operation is subjected to a high voltage direct current field in combination with thermal fluctuations and/or a build up of a substantial thermal gradient within the insulation. The dielectric fluid employed shall exhibit a high viscosity index such that it during impregnation has a sufficiently low viscosity, i.e. a viscosity deemed suitable and technically and economically favourable for impregnation, and that it after impregnation has a high viscosity and elasticity, i.e. a viscosity that ensures that it during operation, will be essentially retained in the porous, fibrous and/or laminated insulation body at all temperatures within the range of temperatures for which the DC-cable is designed to operate. The DC-cable shall thus comprise a dielectric fluid with a sufficiently low viscosity prior to and during impregnation to ensure stable flow properties and flow behaviour within these ranges, and which exhibits a substantial change in viscosity upon impregnation, i.e. a change in the order of hundreds of Pas or more. A DC-cable impregnated with a fluid exhibiting such high viscosity index will provide an opportunity for a substantial reduction in the lengthy time

consuming batch-treatment for impregnation of the insulation system. Thereby providing a potential for a substantial reduction in the production time and thus the production costs. The reliability, low maintenance requirements and long working life of conventional DC-cables, comprising an impregnated paper-based insulation shall be maintained or improved. That is, the DC-cable shall have stable and consistent dielectric properties and a high and consistent electric strength and, as an extra advantage, open for an increase in the electrical strength and thus allow an increase in operation voltages, improved handleability and robustness of the cable.

SUMMARY OF THE INVENTION

According to the present invention it is an object to provide a dielectric gelling composition, which exhibits a thermo-reversible liquid-gel transition at a high temperature with the desirous features discussed in the foregoing. This is, for a dielectric gel according to the preamble of claim 1, accomplished by the features of the characterizing part of claim 1. Further developments of the dielectric gel according to the present invention are characterized by the features of the additional claims 2 to 16.

According to another aspect of the present invention it is an object to provide a method for manufacturing such a dielectric gelling composition. This is for the method according to the preamble of claim 17 accomplished by the features of the characterizing part of claim 17. Further developments of the method for manufacturing such a dielectric gelling composition according to the present invention are characterized by the features of the additional claims 18 to 21.

According to still another aspect of the present invention its an object to provide an insulated electric device comprising such a dielectric gelling composition as impregnant in its impregnated insulation system. This is for an electric device according to the preamble of claim 22 accomplished by the features of claim 22 . Further developments of the electric device according to the present invention are characterized by the features of the additional claims 22 to 26. According to another aspect of the present invention it is an object to provide a method for manufacturing such an insulated electric device. This is for the method according to the preamble of claim 30 accomplished by the features of the characterizing part

of claim 30. Further developments of the method are characterized by the features of the additional claims 31 to 35.

DESCRIPTION OF THE INVENTION

The primary object is accomplished with a dielectric gelling composition, exhibiting a thermo-reversible liquid-gel transition at a transition temperature, T_t , wherein the gel comprises an oil and a gelator comprising a block copolymer comprising an olefin based block and at least one further block comprising aromatic rings in its backbone structure, wherein each one of the two blocks has a molecular weight of more than 3000 g/mole, and the block with aromatic rings in its backbone structure exhibits a rigid backbone structure and a temperature dependent solubility in the oil. Depending on the ratio between the olefin based block (A) which typically constitutes the base of the block copolymer and the block (B) comprising aromatic rings in its backbone structure, the polymer compound can either be a di-block copolymer or a tri-block copolymer with the olefinic block (A) as midblock surrounded on both sides with end blocks consisting of the block (B) comprising aromatic rings in its backbone structure. Preferably, the block with aromatic rings in its backbone structure has a molecular weight of from 5000 to 300 000 g/mole and the olefin based block has a preferred molecular weight of from 3000 to 500 000 g/mole. The gelling composition when in the gelled state typically comprises a gelled network with physical cross-links, where the cross-links comprise regions formed by the block with aromatic rings at temperatures below the liquid-gel transition temperature T_t . These cross-links provide both the mechanical and the dielectric strength to the gelling composition and thus contribute both to the improved mechanical and electrical properties of the insulation system and also to the increased stability of these properties. The gelled network with its physical cross-links is typically formed at temperatures below the transition temperature, which for a gelling composition according to the present invention is below 120 °C, typically the liquid-gel transition temperature T_t is within the range of from 20 °C to 120 °C and preferably is within the range of from 30 °C to 100 °C.

A suitable polymer for block (B) with aromatic rings in its backbone structure is;

- a polyimide or a polyimide based polymer, i.e. a polymer comprising polyimide groups in its backbone structure;
- a polyurethane or a polyurethane based polymer, i.e. a polymer comprising polyurethane groups in its backbone structure;
- a polyphenylene or a polyphenylene based polymer, i.e. a polymer comprising polyphenylene groups in its backbone structure,
- an aromatic polyamide or a polymer based on aromatic polyamide, i.e. a polymer comprising aromatic polyamide groups in its backbone structure,
- a bisphenol-A-epoxy or a polymer based on a bisphenol-A-epoxy, i.e. a polymer comprising aromatic bisphenol-A-epoxy groups in its backbone structure, or
- a phenol-formaldehyde or a polymer based on a phenol-formaldehyde, i.e. a polymer comprising aromatic phenol-formaldehyde groups in its backbone structure.

Typically the polymer for the block (B) is thermally stable and electrically insulating such that it contributes to an increased thermal stability and electric strength of the dielectric gelling composition. Further it shall have a limited solubility in the oil at temperatures below the transition temperature T_i but be substantially dissolved at temperatures above the transition temperature T_i . It shall be noted that T_i typically is a narrow range of temperatures. Preferably the B block polymer has a limited solubility in the oil at ambient temperatures and in some cases up to 50 °C or 60 °C but is substantially dissolved at temperatures above 80 °C. Thus the gelling composition will come to exhibit a transition temperature or a narrow transition range of temperatures in the temperature range of from 30 °C to 100 °C.

The olefin based A block typically comprises an ethylene/butylene block but can also comprise other suitable olefines such as butadiene.

The copolymer comprised in the gelling composition according to the present invention has typically been synthesized by a condensation reaction of a hydroxyl or amine terminated ethylene/butylene or butadiene with polymers containing chemical moieties towards hydroxyl or amine groups. Examples of such moieties reactive towards hydroxyl groups are carboxylic acids, acid chlorides, anhydrides and isocyanates. Thus, according to the present invention, suitable polymers to be included in the di or tri block polymer with an ethylene/butylene block in order to obtain a more thermally stable block copolymer than the prior art styrenic block copolymer, comprise polyimid, polyphenylene oxide, polyurethane, aromatic polyamide, bisphenol-A-epoxy, phenol-formaldehyde and the like. Depending on

the ratio between the olefin based block (A) precursor and the block (B) precursor added to the condensation reaction, either a di-block copolymer or a tri-block copolymer with the olefinic block (A) as midblock surrounded on both sides with end blocks consisting of the block (B) comprising aromatic rings in its backbone structure can be formed.

The dielectric gelling composition and the oil interact to develop a three dimensional, physically cross-linked network at temperatures below the transition temperature T_i . Typically the transition temperature T_i is a narrow range of temperatures above 20 °C and below 120 °C, preferably of from 30 °C to 100 °C. The gelled network with physical cross-links comprises regions formed by the block with aromatic rings at temperatures below the liquid-gel transition temperature T_i . These cross-links provide both the mechanical and the dielectric strength to the gelling composition and thus contribute both to the improved mechanical and electrical properties of the insulation system and also to the increased stability in properties. The network increases the viscosity index of the oil such that the gelled network in the oil according to the present invention at temperatures below the transition temperature T_i exhibits the properties of an highly viscous elastic or viscoelastic gel. Another advantage of the gelling composition used according to the present invention is that the gelling kinetics can be modified by altering the blocks or the content of the block copolymer added to the oil, which opens for a delayed significantly slower gelling if so desired, this delay can in some cases exceed 24 h.

An insulated electric device such as a DC-cable having at least one conductor and an impregnated insulation system, wherein the insulation system comprises a solid electrically insulating dielectric part with a porous, fibrous and/or laminated structure impregnated with a dielectric gelling composition comprising an oil and a gelator, comprising a block copolymer with an olefin based block and exhibiting a thermo-reversible liquid-gel transition at a transition temperature, T_i , wherein the gelling composition at temperatures below T_i is in a highly viscous elastic gelled state and, at temperatures above T_i , is in a liquid easy flowing essentially Newtonian state, comprises according to the present invention a block copolymer with an olefin based block and at least one further block comprising aromatic rings in its backbone structure, wherein each one of the two blocks has a molecular weight of more than 3000 g/mole, and the block with aromatic rings in its backbone structure exhibits a rigid backbone structure and a temperature dependent solubility in the oil. Preferably the block with aromatic rings in its backbone structure has a molecular weight of

from 5000 to 300 000 g/mole while the olefin based block has a molecular weight of from 3000 to 500 000 g/mole. The gelling composition when in the gelled state comprises, as already described in detail in the foregoing, a gelled network with physical cross-links comprising regions formed by the block with aromatic rings at temperatures below the liquid-gel transition temperature T_i . The transition temperature is typically below 120 °C and suitably within a range of from 30°C to 100 °C.

According to one embodiment the dielectric gelling composition is selected such that it comprises groups or further additives that interact with the surface of the porous and/or laminated structure. An interaction between the dielectric gelling composition and the surface of the porous and/or laminated structure can provide conditions that increase the oil penetration into voids and capillary interstices within the porous and/or laminated structure upon filling or that increase the oil retention within the porous and/or laminated structure upon operation at a high temperature, fluctuating temperatures and/or under a substantial temperature gradient. The interaction with the solid parts of the insulation can thus depending on its nature result in an improved wetting which shortens the impregnation time period due to an increase in the oil penetration into voids and capillary interstices within the porous and/or laminated structure upon filling. The interaction can also under other circumstances increase the oil retention within the porous and/or laminated structure upon operation at a high temperature, fluctuating temperatures and/or under a substantial temperature gradient.

According to one embodiment the insulation system comprises a surfactant to further enhance the wetting during impregnation. This provides an opportunity to further shorten the impregnation time to and to use solid part in the insulation system with finer pores, voids or other interstices to be filled with impregnant. The surfactant can be added either to the gelling composition, i.e. the impregnant or the solid porous, fibrous and/or laminated part to be insulated as deemed suitable from case to case.

According to one further embodiment the gelling composition comprises fine dielectric particles with a particle size in the nanometer range trapped in or bonded to the network.

A method of manufacturing an insulated electric device wherein a solid electrically insulating dielectric part with a porous, fibrous and/or laminated structure comprised in the insulation system of the device is impregnated with a dielectric gelling composition comprising a dielectric fluid and a gelator, comprising a block copolymer with

an olefin based block and exhibiting a thermo-reversible liquid-gel transition at a transition temperature, T_i , wherein the gelling composition at temperatures below T_i is in a highly viscous elastic gelled state and, at temperatures above T_i , is in a liquid easy flowing essentially Newtonian state, comprises according to the present invention a step in which a gelling composition comprising a polymer compound, consisting of a block copolymer comprising an olefin based block and at least one further block comprising aromatic rings in its backbone structure, wherein each one of the two blocks has a molecular weight of more than 3000 g/mole, and the block with aromatic rings in its backbone structure exhibits a rigid backbone structure and a temperature dependent solubility in the oil, is prepared. The polymer compound is either added to the gelling composition prior to impregnation or the solid part of the insulation system, which then typically is pretreated, impregnated or coated, with the polymer compound prior to impregnation.

A DC-cable according to the present invention typically comprises from the center and outwards;

- a conductor of any desired shape and constitution, such as a stranded multi-wire conductor, a solid conductor or a sectional conductor;
- a first semi-conducting shield disposed around and outside the conductor and inside the conductor insulation;
- a wound and impregnated insulation according to the present invention with a dielectric electrically insulating solid part exhibiting a porous and/or laminated structure as described in the foregoing impregnated with an oil;
- a second semi-conducting shield disposed outside the conductor insulation; and
- an outer protective sheath. Also, the two semi-conducting shields are typically wound and impregnated insulation according to the present invention, with a dielectric electrically insulating solid part exhibiting a porous and/or laminated structure as described in the foregoing impregnated with an oil based gelling composition. The cable can when deemed appropriate be complemented with reinforcing and a sealing compound or a water swelling powder for filling any interstices in and around the conductor, other metal/polymer interfaces may be sealed in order to prevent water from spreading along such interfaces.

To ensure the long term stability of the improved electrical and mechanical properties a gasabsorbing additive is included in the insulating system. A suitable

gasabsorbing additive is a low molecular polyisobutene with a molecular weight less than 1000 g/mole.

A DC-cable according to the present invention is, through the improved electrical and mechanical strength of the gelled network formed at temperatures below the transition temperature and the long term stability of these improved properties also at elevated temperatures approaching the transition temperature, ensured long term stable and consistent dielectric properties and a high and consistent electric strength as good as or better than for any conventional DC-cable comprising such impregnated porous and/or laminated body. This is especially important due to the long life such installations typically are designed for, and the limited access for maintenance to such installations. The special composed block copolymers used as gelling additives and oils, provide gelling impregnants, which ensure the long term stable properties of the insulation system also when used at elevated temperatures, at excessive thermal fluctuations and/or under thermal gradients. This opens for a capability to allow an increase in the operation load both in regards of increased voltages and current densities. Also, the temperature sensitivity during production can be substantially reduced by a suitable design of the block copolymer used and matching of oil and any other components added to the gelator system, which opens for a delayed gelling, thereby reducing sensitivity of the post-filling step.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention shall be described more in detail under reference to the drawings and examples. Figure 1 shows a cross-section of a typical DC-cable for transmission of electric power comprising a wound and impregnated insulation according to the present invention

DESCRIPTION OF PREFERRED EMBODIMENTS, EXAMPLES.

The DC-cable according to the embodiment of the present invention shown in figure 1 comprises from the center and outwards;

- a stranded multi-wire conductor 10;

- a first semi-conducting shield 11 disposed around and outside the conductor 10 and inside a conductor insulation 12;
- a wound and impregnated conductor insulation 12 comprising a gelling additive as described in the foregoing;
- a second semi-conducting shield 13 disposed outside the conductor insulation 12;
- a metallic screen 14; and
- a protective sheath 15 arranged outside the metallic screen 14. The cable is further complemented with a reinforcement in the form of metallic, preferably steel, wires outside the outer extruded shield 13, a sealing compound or a water swelling powder is introduced in any interstices in and around the conductor 10.

The dielectric gelling composition of the present invention is applicable for any arbitrary DC-cable with an insulation system comprising a solid porous or laminated part impregnated with a dielectric fluid or mass. The application of the present invention is independent of conductor configuration. It can also be used with DC-cables having an insulation system of this type comprising any arbitrary functional layer(s) and irrespective of how these layers are configured. Its application to DC-cables of this type is also independent of the configuration of the system for transmission of electric power in which the cable is included.

The DC-cable according to the present invention can be a single multi-wire conductor DC-cable as shown in Figure 1, or a DC-cable with two or more conductors. A DC-cable comprising two or more conductors can be of any known type with the conductors placed side-by-side in a flat cable arrangement, or in a two conductor arrangement with one first central conductor surrounded by a concentrically arranged second outer conductor. The outer conductor is typically arranged in the form of an electrically conductive sheath, screen or shield, typically a metallic screen not restricting the flexibility of the cable.

A DC-cable according to the present invention is suitable for use in both bipolar and monopolar DC-systems or installations for transmission of electric power. A bipolar system typically comprises two or more associated single conductor cables or at least one multiconductor cable, while a monopolar installation has at least one cable and a suitable current return path arrangement.

EXAMPLE 1

An ethylene/butylene polymer terminated at both ends with hydroxyl groups was dissolved in p-xylene and heated to 150 °C under stirring and nitrogen atmosphere. A poly-(2,6-dimethyl-phenylene oxide) terminated at one end with a cyclic acid anhydride was added to the solution under stirring. The mixture was kept at 150 °C for 60 minutes. The mixture was subsequently cooled to room temperature. The polymer was precipitated in methanol, washed with cyclohexane and dried. 4 % by weight of the resulting polymer was added to a naphtenic mineral oil and the blend was heated to 120 °C and kept at this temperature for 60 minutes. Substantially all polymer was dissolved. The blend was cooled and the blend or oil composition exhibited a liquid-gel transition in the temperature range 50 °C to 100 °C.

EXAMPLE 2

An ethylene/butylene polymer terminated at both ends with hydroxyl groups was dissolved in trichlorobenzene and heated to 150 °C under stirring and nitrogen atmosphere. An epoxy prepolymer terminated at one end with an epoxide group was added to the solution under stirring. The mixture was kept at 150 °C for 80 minutes. The mixture was subsequently cooled to room temperature. The polymer was precipitated in methanol, washed with acetone and dried. 6 % by weight of the resulting polymer was added to a naphtenic mineral oil and the blend was heated to 120 °C and kept at this temperature for 60 minutes. Substantially all polymer was dissolved. The blend was cooled and the blend or oil composition exhibited a liquid-gel transition in the temperature range 30 °C to 100 °C.

CLAIMS

1. A dielectric gelling composition, exhibiting a thermo-reversible liquid-gel transition at a transition temperature, T_i , wherein the gelling composition comprises an oil and a gelator comprising a polymer compound with an olefin based block, **characterized** in that the polymer compound consists of a block copolymer comprising an olefin based block and at least one further block comprising aromatic rings in its backbone structure, wherein each one of the two blocks has a molecular weight of more than 3000 g/mole, and that the block with aromatic rings in its backbone structure exhibits a rigid backbone structure and a temperature dependent solubility in the oil.
2. A dielectric gelling composition according to claim 1, **characterized** in that the block with aromatic rings in its backbone structure has a molecular weight of from 5000 to 300 000 g/mole
3. A dielectric gelling composition according to claim 1 or 2, **characterized** in that the olefin based block has a molecular weight of from 3000 to 500 000 g/mole.
4. A dielectric gelling composition according to any of claims 1 to 3, **characterized** in that the gelling composition when in the gelled state comprises a gelled network with physical cross-links comprising regions formed by the block with aromatic rings at temperatures below the liquid-gel transition temperature T_i .
5. A dielectric gelling composition according to claim 4, **characterized** in that the gelling composition when in the gelled state comprises a gelled network with physical cross-links comprising regions formed by the block with aromatic rings at temperatures up to 120 °C.
6. A dielectric gelling composition according to claim 5, **characterized** in that the gelling composition when in the gelled state comprises a gelled network with physical cross-links comprising regions formed by the block with aromatic rings at temperatures up to 100 °C.

7. A dielectric gelling composition according to any of the preceding claims, **characterized** in that the liquid-gel transition temperature T_l is within the range of from 20°C to 120 °C.
8. A dielectric gelling composition according to claim 7, **characterized** in that the liquid-gel transition temperature T_l is within the range of from 30°C to 100 °C.
9. A dielectric gelling composition according to any of the preceding claims, **characterized** in that the block with aromatic rings in its backbone structure is a polyurethane or a polyurethane based polymer.
10. A dielectric gelling composition according to any of claims 1 to 8, **characterized** in that the block with aromatic rings in its backbone structure is a polyphenylene or a polyphenylene based polymer.
11. A dielectric gelling composition according to any of claims 1 to 8, **characterized** in that the block with aromatic rings in its backbone structure is a polyimide or a polyimide based polymer
12. A dielectric gelling composition according to any of claims 1 to 8, **characterized** in that the block with aromatic rings in its backbone structure is an aromatic polyamide or a polymer based on aromatic polyamide.
13. A dielectric gelling composition according to any of claims 1 to 8, **characterized** in that the block with aromatic rings in its backbone structure is a bisphenol-A-epoxy or a polymer based on a bisphenol-A-epoxy.
14. A dielectric gelling composition according to any of claims 1 to 8, **characterized** in that the block with aromatic rings in its backbone structure is a phenol-formaldehyde or a polymer based on a phenol-formaldehyde.

15. A dielectric gelling composition according to any of the preceding claims, **characterized** in that the olefin based block is a ethylene/butylene block.
16. A dielectric gelling composition according to any of claims 1 to 14, **characterized** in that the block is a butadiene block.
17. A method of manufacturing a gelling composition, exhibiting a thermo-reversible liquid-gel transition at a transition temperature, T_t , wherein the gel comprises an oil and a gelator comprising a polymer compound with an olefin based block, **characterized** in that a block comprising aromatic rings in its backbone structure and having a molecular weight of more than 3000 g/mole is added to an olefin based block having a molecular weight of more than 3000 g/mole by means of a condensation reaction carried out at an elevated temperature.
18. A method according to claim 17, **characterized** in that
- an olefin based block or its precursor is dissolved in an oil or other hydrocarbon based dielectric fluid,
 - a block comprising aromatic rings in its backbone structure or its precursor is added to the blend of the olefin comprising block and oil or other hydrocarbon based dielectric fluid,
 - the blend is kept at a temperature above the transition temperature for a sufficient period of time, such that a block copolymer with a block comprising aromatic rings in its backbone structure and an olefin based block is formed by means of a condensation reaction, and that the blend is transformed to a gelling composition which upon cooling to a temperature below the transition temperature is gelled by a gelled network with physical cross-links comprising regions formed by the block with aromatic rings.
19. A method according to claim 17, **characterized** in that an olefin based block terminated at one or both ends with a hydroxyl group is dissolved in a solvent, that a block comprising aromatic rings in its backbone structure and terminated with functional groups being reactive towards hydroxyl groups such as carboxylic acids, acid chlorides, anhydrides or isocyanates, is added to the solution, that the solution is kept at sufficient temperature for a sufficient period of time such that a block copolymer is formed by means of a condensation

reaction where a block comprising aromatic rings in its backbone structure is added to an olefin based block, and that the resulting block copolymer is added to an oil at a temperature above the transition temperature and kept at this temperature for a sufficient time such that the oil is transformed to a gelling composition which upon cooling to a temperature below the transition temperature is gelled by a gelled network with physical cross-links comprising regions formed by the block with aromatic rings.

20. A method according to claim 17, 18 or 19, **characterized** in that the condensation reaction is carried out at a temperature above 100 °C and that the solution or blend containing precursors for both blocks is kept at this temperature for more than 30 minutes.

21. A method according to claim 17, 19 or 20, **characterized** in that the resulting block copolymer is added to the oil at a temperature above 100 °C and that the oil polymer blend is kept at this temperature for more than 30 minutes.

22. An insulated electric device having at least one conductor and an impregnated insulation system, wherein the insulation system comprises a solid electrically insulating dielectric part with a porous, fibrous and/or laminated structure impregnated with a dielectric gelling composition comprising an oil and a gelator, comprising a block copolymer with an olefin based block and exhibiting a thermo-reversible liquid-gel transition at a transition temperature, T_i , wherein the gelling composition at temperatures below T_i is in a highly viscous elastic gelled state and, at temperatures above T_i , is in a liquid easy flowing essentially Newtonian state, according to any of claims 1 to 16, **characterized** in that the block copolymer comprises an olefin based block and at least one further block comprising aromatic rings in its backbone structure, wherein each one of the two blocks has a molecular weight of more than 3000 g/mole, and that the block with aromatic rings in its backbone structure exhibits a rigid backbone structure and a temperature dependent solubility in the oil.

23. An insulated electric device according to claim 22, **characterized** in that the block with aromatic rings in its backbone structure has a molecular weight of from 5000 to 300 000 g/mole

24. An insulated electric device according to claim 22 or 23, characterized in that the olefin based block has a molecular weight of from 3000 to 500 000 g/mole.
25. An insulated electric device according to any of claims 22 to 24, characterized in that the gelling composition when in the gelled state comprises a gelled network with physical cross-links comprising regions formed by the block with aromatic rings at temperatures below the liquid-gel transition temperature T_l .
26. An insulated electric device according to claim 25, characterized in that the gelling composition when in the gelled state comprises a gelled network with physical cross-links comprising regions formed by the block with aromatic rings at temperatures up to 120 °C.
27. An insulated electric device according to claim 26, characterized in that the liquid-gel transition temperature T_l is within the range of from 30°C to 100 °C.
28. An insulated electric device according to any of claims 22 to 27, characterized in that the gelling composition comprises fine dielectric particles with a particle size in the nanometer range trapped in or bonded to the network.
29. An insulated electric device according to any of claims 22 to 28, characterized in that the gelling composition comprises a surfactant.
30. Method of manufacturing an insulated electric device wherein a solid electrically insulating dielectric part with a porous, fibrous and/or laminated structure comprised in the insulation system of the device is impregnated with a dielectric gelling composition comprising a dielectric fluid and a gelator, comprising a block copolymer with an olefin based block and exhibiting a thermo-reversible liquid-gel transition at a transition temperature, T_l , wherein the gelling composition at temperatures below T_l is in a highly viscous elastic gelled state and, at temperatures above T_l , is in a liquid easy flowing essentially Newtonian state, according to any of claims 22 to 29, characterized in that a

gelling composition comprising a polymer compound, consisting of a block copolymer comprising an olefin based block and at least one further block comprising aromatic rings in its backbone structure, wherein each one of the two blocks has a molecular weight of more than 3000 g/mole, and that the block with aromatic rings in its backbone structure exhibits a rigid backbone structure and a temperature dependent solubility in the oil, is prepared.

31. A method according to claim 30, **characterized** in that the polymer compound is added to the gelling composition prior to impregnation.

32. A method according to claim 30, **characterized** in that the solid part of the insulation system is pretreated with the polymer compound prior to impregnation.

33. A method according to any of claims 30 to 32, **characterized** in that the impregnation is carried out in the presence of a surfactant.

34. A method according to claim 33, **characterized** in that the surfactant is added to the gelling composition prior to impregnation.

35. A method according to claim 33, **characterized** in that the solid part of the insulation system is pretreated with the surfactant prior to impregnation.

36. A dielectric gelling composition according to any of claims 1 to 16, **characterized** by a gasabsorbing additive, such a low molecular polyisobutene.

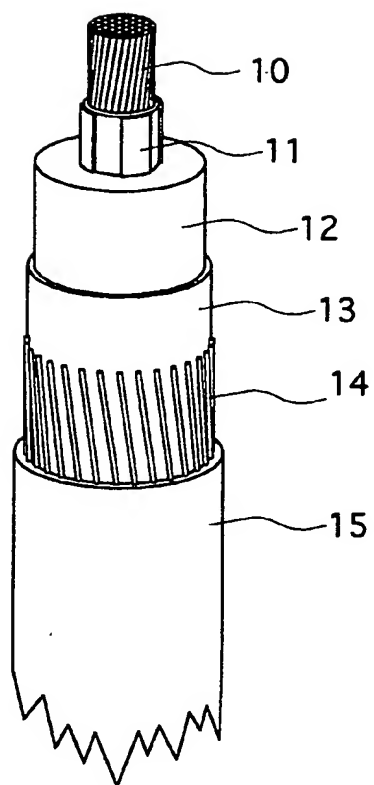


Fig 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/SE 98/02311

| A. CLASSIFICATION OF SUBJECT MATTER IPC 6 H01B3/20 | | |
|---|--|--|
| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 H01B | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | |
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| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
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| <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. | | |
| * Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family | | |
| Date of the actual completion of the international search 31 March 1999 | | Date of mailing of the international search report 12/04/1999 |
| Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | | Authorized officer Stienon, P |

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